MASTER

RECENT DEVELOPMENTS IN THORIUM FUEL PROCESSING*

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RELEASED FOR ANNOUNCEMENT
IN NUCLEAR SCIENCE ABSTRACTS

ABSTRACT

Three head-end processes are being developed for thorium-base power reactor fuels. The processes are: shear-leach for metal-clad oxides and either grind-leach or burn-leach for graphite-base High-Temperature Graphite Reactor (HTGR) fuels. The shear-leach process is being used in the first commercial fuel processing plant; further development is necessary before selecting a process for graphite-base reactor fuels.

During the past year, shear-leach studies were made on secondary problems associated with the process. These studies include calculation of the fuel temperature during the various process steps, measurement of the release of krypton and tritium during processing, the zirconium-metal fines safety problem, development of an instrument for monitoring hulls for leaching losses, and shearing tests on second-generation fuel elements.

* Research sponsored by the U.S. Atomic Energy Commission under contract with the Union Carbide Corporation.

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JUN 27 1966

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Grind-leach process studies were done in the laboratory and in small-engineering-scale experiments with unirradiated HTGR fuel. Grinding, leaching, and washing conditions have been determined for satisfactory recovery of the uranium and thorium. Engineering problems associated with grinding graphite and filtering graphite slurries are also being studied.

For the burn-leach process, estimates were made of the fission-product activity in the off-gas from a fluidized-bed burner. Fission product behavior and other problems associated with burn-leach processing are being studied in hot-cell experiments.

Other studies include protactinium recovery by adsorption on unfired Vycor glass, and chemical and engineering studies of a close-coupled processing plant in which simplified, low-cost, limited-decontamination processing methods are used to prepare feed materials for an associated fuel-fabrication plant operated by remote control.

1. INTRODUCTION

The recent development work at Oak Ridge National Laboratory (ORNL) on thorium fuel processing has been primarily concerned with head-end processes and with conceptual studies of close-coupled processing and fabrication plants. The purpose of this report is to summarize the information developed in the past year.

For the metal-clad (U-Th)O₂ fuels, a shear-leach process is the preferred head-end process and is very nearly fully developed for industrial application. We are now doing work on secondary problems that deal with operating safety and convenience and problems associated with newer fuel types. The Nuclear Fuel Services (NFS) shear-leach

operating experience will be available soon; therefore, our program will be de-emphasized in the near future.

For the graphite-base High-Temperature Gas-Cooled Reactor (HTGR) fuels, we are developing both a burn-leach process and a grind-leach process. Each process is feasible but has several major problems that require solution before the processes can be considered for plant-scale use. The principal problem in the burn-leach process is cleanup of the burner off-gas. Cleanup is required to remove fission products that are volatilized at elevated temperatures in the burner and to remove entrained particulate material. For the grind-leach process, the problems are storage of highly active graphite waste and the extra head-end steps to remove soluble organic compounds before solvent extraction. At present, we prefer the burn-leach process and are developing the grind-leach process primarily as a backup for fuels having refractory coatings, such as SiC and Al₂O₃, on the fuel particles. Obviously, the head-end process selection for HTGR fuels may be strongly influenced by factors such as plant capacity, or by major changes in fuel design. For example, will the fuel particles be easily separated from the structural graphite? What scheme will be used to separate bred ²³³U from the ²³⁵U particle which contains ²³⁶U after irradiation? Since the HTGR concept is several years away from large-scale, multireactor exploitation, it is premature to make a choice between the two head-end processes.

Solvent extraction, using the Acid Thorex process,¹ is considered the best method of recovering uranium and thorium. No development work has been done recently on the Acid Thorex process, although some work will be done in the near future as part of our close-coupled process studies.

The results of the initial phase close-coupled process program indicate that continuous solvent extraction is the best processing choice, even for low-decontamination processing. Preliminary cost information indicates that processing in a small, close-coupled plant may cost no more than the published costs for processing the Indian Point ThO₂ core in the Nuclear Fuel Services plant. This is an encouraging comparison for such a small plant. However, thorium processing and remote fabrication are still more expensive ($\geq 30\%$) than the low-enrichment uranium fuel cycle for water-cooled reactors. Having demonstrated a case for close-coupled plants, we will now study advanced converters, such as the HTGR's, where the advantages of thorium fuels over low-enrichment uranium can be realized.

2. SHEAR-LEACH PROCESSING

The shear-leach process has been intensively investigated²⁻⁵ at ORNL and is being used by Nuclear Fuel Services to process power reactor fuels clad with stainless steel or zirconium alloys and containing cores of UO₂, ThO₂-UO₂, U-Mo alloy, or Th-U alloy.

The process consists of several basic steps (Fig. 1): fuel element disassembly, shearing the fuel into short lengths to expose the core, loading sheared fuel into baskets, leaching, monitoring the leached cladding (hulls), and waste packaging and disposal. Shear-leach has been successfully demonstrated with unirradiated prototype thorium-uranium and uranium-bearing fuels on an engineering scale and with irradiated fuel pin samples in hot-cell experiments.⁵ In the engineering-scale demonstration,⁵ perforated baskets containing 18 to 36 kg of sheared unirradiated ThO₂-UO₂ fuel were leached

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Fig. 1. Shear-Leach Process for Spent Reactor Fuels.

in 8 to 26 hr with losses of only 0.1%. Unirradiated UO_2 leaches in about one-eighth the time required for $\text{ThO}_2\text{-UO}_2$ under roughly comparable conditions, and hot-cell tests demonstrated that irradiated $\text{ThO}_2\text{-UO}_2$ dissolves significantly faster than unirradiated fuel.⁶ Other tests⁷ showed that from 1 to 5% of the Zircaloy cladding as well as 60 to 80% of the -10 mesh Zircaloy fines (less than 1% of the cladding weight) generated by shearing dissolves in the boiling leachant [$13\text{ }M\text{ HNO}_3\text{--}0.04\text{ }M\text{ HF--}0.4\text{ }M\text{ Al(NO}_3)_3$]. The presence of the dissolved zirconium decreased the dissolution rate of the thorium but not enough to seriously affect the overall leaching time.

Since the primary development of the shearing and leaching process is completed, recent shear-leach development work has been on secondary items. The recent investigations are discussed in the following sections.

2.1 Estimation of the Fuel Temperature During Shear-Leach Processing

The internally generated heat from fission product decay may result in high fuel temperatures detrimental to the fuel or equipment during shear-leach processing. This was evaluated by computer calculations for fuel irradiated to burnups of 8,000 to 50,000 Mwd/metric ton at specific powers of 10 to 70 kw/kg with cooling times ranging from 180 to 1080 days. Cooling was by radiation and natural convection to the surrounding medium. In the calculations, a Yankee Atomic fuel subassembly was selected to represent a typical power reactor fuel, but the results are equally applicable to thorium oxide fuel. The subassembly consisted of a square bundle of thirty-six 0.302-in.-OD by 120-in.-long UO_2 -filled stainless steel fuel rods on 0.422-in. centers and was assumed to be irradiated to a burnup of 20,000 Mwd/metric ton at a specific power

of 23 kw/kg and cooled 180 days. The fuel temperature was calculated for the vertical fuel subassembly in the storage canal, for the horizontal fuel element in air in the dismantling cell and in air in the shear feed envelope, and finally as sheared fuel stored in air in a 16-basket array with baskets of 5-, 7.75-, and 10-in.-ID (Table 1). The results indicate there is no danger that the fuel or clad will melt. With the possible exception of the calculated temperature of 548°F for the hottest fuel in the shear envelope, overheating should not be a serious problem for the shearing equipment. In any case, the temperature of the fuel in the shear envelope could be lowered considerably by forced air cooling.

2.2 Krypton and Tritium Release During Shear-Leach Processing

Hot-cell experiments were conducted to measure the release of krypton and tritium during shear-leach processing.⁸ Several stainless-steel-clad prototype Consolidated Edison fuel samples containing high-density (96% of theoretical) pellets of 96% ThO₂—4% fully enriched UO₂ irradiated to 25,000 Mwd/metric ton were sheared in special hot-cell equipment. The first cut released 0.03% of the calculated amount of tritium and 0.5% of the ⁸⁵Kr; multiple shearing into 1/2-in. segments released a maximum of 0.26% of the tritium and 1.07% of the ⁸⁵Kr. Tritium was released very slowly by the sheared material on standing. Only 0.26% of the tritium escaped in the dissolver off-gas when the sheared fuel was dissolved in boiling 13 M HNO₃—0.1 M Al(NO₃)₃—0.05 M HF. The balance of the ⁸⁵Kr was released during dissolution but was not measured. Tritium oxide distillation during boildown of the dissolver solution to remove excess acid was directly proportional to the amount

Table 1. Calculated Fuel Temperatures During Shear-Leach Processing of Stainless-Steel-Clad UO_2 Fuel

Operation or Process Step	Fuel Temperature ($^{\circ}\text{F}$)			
	Typical Power Reactor Fuel ^a		Highly Irradiated Short-Cooled Fuel ^b	
Canal storage	71.5		75.5	
Mechanical disassembly	150		191	
Shear-feed envelope	350		548	
	<u>Centerline</u>	<u>Surface</u>	<u>Centerline</u>	<u>Surface</u>
Sheared fuel stored in 16-basket array:				
5-in.-ID baskets	491	324	852	548
7-3/4-in.-ID baskets	720	453	1244	773
10-in.-ID baskets	924	575	1586	979

^a Burnup 20,000 Mwd/metric ton at 23 kw/kg, 180-day-cooling.

^b Burnup 50,000 Mwd/metric ton at 70 kw/kg, 180-day-cooling.

evaporated. After rectification of the acid distillate and high-level extraction wastes, most of the tritium would eventually be discharged as a low- or intermediate-level waste stream, thus complicating low-activity-level waste disposal. Extrapolation of these data indicates that 1 curie of tritium would be released in the head-end off-gas for each metric ton of heavy metals sheared and dissolved, and hence should not be a significant off-gas problem.

Similar gas release experiments were made with prototype PWR fuel specimens containing high-density (93% of theoretical) UO_2 pellets clad in Zircaloy-2 and irradiated to 40,000 Mwd/metric ton. These fuel pins were also sheared into 1/2-in. segments and the exposed fuel was dissolved in 4 M HNO_3 . Shearing released 7.43% of the calculated fission yield of tritium, and only 0.13% of the total tritium was carried by the dissolution off-gas. Total release of tritium during the shearing and leaching of 1 metric ton of UO_2 fuel would amount to about 37 curies, which does not appear to be a significant off-gas hazard.

The amount and composition of the undissolved residue after leaching and after the feed adjustment boildown were determined for the pins containing $\text{ThO}_2\text{-UO}_2$. The leaching residue amounted to 0.58 wt % of the original fuel and consisted principally of silica, alumina, and corrosion products with 0.74 wt % Mo, 0.23 wt % Zr-Nb, 0.01 wt % Sb, and insoluble uranium and thorium representing a 0.05% loss. Antimony was the principal radiation emitter. During feed-adjustment boildown, a residue precipitated that represented about 0.6% of the weight of the original fuel and contained molybdenum and zirconium plus a uranium loss of 0.02% and a thorium loss of 0.05%.

2.3 Safety Studies on Shear-Leach Processing of Zircaloy-2—Clad Fuel

The safety problems associated with the zirconium metal fines produced by abrasive-disk sawing and produced by shearing the fuel rods are being investigated.

Zircaloy-2 particles produced by both wet and dry abrasive cutting and containing the abrasive particles produced by disk wear in a volumetric ratio of 1 part Zircaloy-2 to 7 parts abrasive particles were subjected to spark-ignition tests in air with a 20,000-v spark. The spark tester did not ignite any of the eight size fractions which ranged from 4760 to $<44 \mu$. Electron probe analysis showed that most of the finer particles had been converted to the oxide in both the wet and dry abrasive cutting tests and were nonreactive. Thus, particles produced in a sawing operation and diluted with abrasive disk debris are considered safe to handle and store.

Shearing an 8-by-8 tube array of Zircaloy-2—clad UO_2 in air produced about one to three low-energy sparks per cut and did not seem to present a fire hazard. Following shearing, the UO_2 was dissolved in 6 M HNO_3 , leaving the Zircaloy-2 fines behind. Analysis of the fines showed that, during shearing and leaching operation, the metal had not been oxidized and only a small amount, if any, of the fines had dissolved. Spark testing in air showed that Zircaloy-2 particles larger than about 150μ in diameter did not react; however, particles smaller than this reacted with increasing violence as the particle size decreased. It is estimated that about 0.45 kg of Zircaloy-2 particles in the potentially hazardous size range of $<400 \mu$ is produced by shearing 1 ton of fuel. As to thorium fuel, from 60 to 80% of the -10 mesh (approximately $<1680 \mu$) Zircaloy particles are dissolved per pass with Thorex reagent⁵;

thus, the fines do not seem to constitute a hazard for processing Zircaloy-2—clad thorium fuel. However, in shear-leach processing of Zircaloy-2—clad UO_2 fuels, these potentially hazardous particles may accumulate in the equipment, since they are not readily dissolved in 6 M HNO_3 . Here, periodic dissolution of the accumulated fines with HNO_3 -HF- $\text{Al}(\text{NO}_3)_3$ solution, or dilution with inert solids and packaging and discarding as a solid waste, may be required.

2.4 Leached-Hull Monitoring

Neutron-activation analysis is being tested for monitoring the leached hulls to detect the presence of unleached fuel.⁹ In this method, the hulls are irradiated with neutrons from a neutron accelerator and the "delayed" neutrons are counted (Fig. 2). Both stainless steel and Zircaloy-2 hulls can be monitored and ^{235}U , ^{233}U , and ^{239}Pu can be readily detected. Tests are being conducted with an 8-in.-diam by 5-ft-tall basket of hulls that contain various amounts of ^{235}U (Fig. 3). The instrument will readily detect as little as 6 mg of ^{235}U in a single hull and is quite sensitive to uniformly distributed fissionable material. Uniform distribution of 100 mg of ^{235}U in the leached hulls in an 8-in. height of 8-in.-diam basket corresponds to a leaching loss of about 0.02% for a fuel containing 2% ^{235}U ; thus, the instrument appears to be sensitive enough and should be quite useful for rapid monitoring of leaching losses. Development of the instrument is continuing.

2.5 Shearing Tests on Second Generation Fuel Elements

The spacing between fuel rods in the fuel elements of the first power reactor cores was, in general, maintained by rigid grids or by brazing the fuel tubes to each

Fig. 2. Leached Hull Monitoring Instrument.

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Basketful of Hulls

Fig. 3. Monitor Response to ^{235}U in Leached Hulls.

other. In the newer fuel elements, these rigid intermediate spacers have been replaced by grids in which the tubes are retained and spaced by small leaf springs or crossed wires. An example of such an assembly is the Elk River Core II ($\text{ThO}_2\text{-UO}_2$) fuel assembly in which the fuel tubes are supported at intermediate points with leaf spring grid assemblies. Since the rods are less rigidly restrained than in the first cores, it was thought that shearing into uniform lengths might be more difficult. An Elk River Core II fuel assembly (porcelain-filled to simulate $\text{ThO}_2\text{-UO}_2$) was successfully sheared into 1-in. sections (Fig. 4). All terminal pieces of tubing were 2 in. long except that two pieces were 2.5 in., one was 3 in., and one was 4 in. long. The leaf springs remained mainly as connected metal strips. Similar results were obtained with even larger assemblies such as the Consolidated Edison Core B fuel element. With these newer fuels, it is necessary to use sharp shear blades with the clearance between fixed and moving blades not exceeding 3 to 5 mils to ensure complete cutting of the grid assemblies and of the perforated element sheath, when present. However, the grid assemblies tend to remain more or less intact and the perforated sheath yields long, flat, metal strips, complicating the shearing operation and basket loading. For this reason, an alternative shearing method, consisting in removing the tubes from the grid-sheath assemblies prior to shearing and then shearing the fuel rods as a loose bundle, has been tested and is satisfactory.

3. GRIND-LEACH PROCESS DEVELOPMENT FOR GRAPHITE-BASE HTGR FUELS

The grind-leach process (Fig. 5) for graphite-base HTGR fuels that contain coated fuel particles consists in grinding or crushing the fuel followed by leaching the

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powdered product with a suitable reagent. The grinding or crushing operation must effect rupture of all of the fuel particle coatings to ensure satisfactory leaching. Hence, the process is applicable to all types of coated-particle HTGR fuels, including those having refractory coatings such as SiC or Al_2O_3 on the particles. Ground fuels containing UO_2 or uranium-thorium carbides can be leached with nitric acid alone; however, those containing ThO_2 or $\text{ThO}_2\text{-UO}_2$ will require nitric acid with a trace of HF as the leachant. After leaching, the residual graphite is separated from the product solution and is washed to ensure maximum recovery of the uranium and thorium. The graphite residue is discarded as a waste. The disposal method will be strongly influenced by the amount of radioactivity remaining in the graphite.

The acidic solutions obtained by leaching carbide-bearing fuel may require additional chemical treatment to destroy the soluble organic compounds derived from carbide hydrolysis, if these compounds prove to be detrimental to solvent extraction performance. After pretreatment, the product solution is concentrated and the uranium and thorium are recovered by solvent extraction.

Laboratory- and small-scale engineering work was conducted with unirradiated Peach Bottom fuel compacts to study crushing, grinding, and leaching. These tests are described in the following sections. Feed preparation and solvent extraction studies on leach liquors derived from carbide-bearing fuels are in progress and hot-cell tests of the process are planned for the future.

3.1 Size Reduction: Crushing and Grinding of HTGR Fuel

Rough crushing of fuel compacts is desirable as a first step to prepare a small-particle-size feed for the final fine grinding or crushing step. Unirradiated Peach

Bottom fuel compacts were rough-crushed by a conventional hammer mill having fixed hammers on a 15-in.-diam by 8-in.-long rotor operating at 845 rpm, with the discharge bars set for 1/8-in.-wide slots. A 75% yield of -6-mesh material was obtained in a single pass. This indicates that production of a 100% -6-mesh product suitable for feed to a fine grinder material should present no problem.

Early work¹⁰ on fine grinding showed that a high-speed hammer mill was excessively worn when HTGR fuels containing SiC-coated particles were ground to 35-mesh (500- μ) particles. Ball milling was also investigated briefly¹¹ but was unattractive because of low grinding rates, the large variation in product size, and the batchwise nature of the operation.

The roll crusher was selected as the fine-grinding method because the maximum dimension of the crushed product is determined quite accurately by the clearance between the rolls; thus, product classification equipment and recycle of oversize material can be avoided. Furthermore, the roll crusher is a very simple, continuously operated machine and should be quite satisfactory for remote use. The size reduction that can be obtained in a roll crusher is a function of the feed particle diameter, the roll diameters, the spacing between rolls (approximately equal to the product diameter), and the coefficient of friction between the feed material and the roll surfaces. This is expressed as the angle of nip,¹² and this angle is of importance for predicting the size reduction ratio per pass. With a mill having 8-in.-diam rolls, the angle of nip was determined to be only 12° for Peach Bottom fuel, primarily because of the low coefficient of friction between the fuel and the smooth steel rolls. The true angle of nip may be somewhat less than 12° because this machine was not sufficiently rigid to maintain

a preset roll spacing. Despite the problems with this machine, 80% of a -6-mesh feed could be crushed to -140 mesh (105 μ) in three passes through the mill, decreasing the roll clearance from 0.045 in. for the first pass to 0.002 in. for the final passes. Reduction of the particle size to -140 mesh was sufficient to ensure rupture of all the fuel particle coatings. The +140 mesh fraction remained close to 20% after the second and third passes and actually increased with the fourth pass through the mill. The explanation for this anomaly is that the roll mill also compresses a great number of smaller particles (primarily from the -140 +325 mesh range) into relatively large but very thin flakes. These flakes were up to 3000 μ in diameter but were only about 50 to 140 μ thick. Therefore, the effectiveness of a roll crusher in fracturing coated particles can be much greater than is indicated by a sieve analysis of the product.

Machine throughput was measured at several values of roll spacing, roll speed, and nominal feed size but the data were inconclusive. A tentative conclusion was that a roll speed of 200 rpm gave a grinding rate for unfueled graphite of 50 to 200 g/min for 2-in.-wide rollers. We estimate that an improved roll crusher with 8-in.-diam by 12-in.-long rolls should be able to -16-mesh HTGR fuel feed to -140 mesh in a single pass at a rate of about 400 kg/day.

On the basis of information obtained with the 8-in.-diam roll crusher, an improved machine was designed and built at ORNL (Fig. 6). The 12-in.-diam rolls of this machine are designed to produce -140-mesh product in a single pass, from -12-mesh material. Two aspects of the design and fabrication received special attention: The roll spacing mechanism was improved to make it very rigid, and a very small clearance

can be maintained between the ends of the rolls and the side plates to minimize bypassing. A heavy coil spring bearing against the moveable roll yoke acts in a direction to force the rolls away from each other; this preloads the spacing adjustment mechanism and helps ensure that there is the least possible change in roll spacing in going from zero throughput to maximum throughput. Preliminary results indicate the machine will grind -4-mesh graphite to -12 mesh at a rate of 120 kg/hr; the final pass to produce -140-mesh material can be done at a rate of about 22 kg/hr.

3.2 Laboratory-Scale Leaching Studies

An investigation aimed at determining optimum conditions for leaching crushed carbide-containing graphite fuels has been initiated in the laboratory. The results obtained thus far showed that the highest uranium and thorium recoveries were achieved with boiling 13 to 16 *M* HNO₃. Fluoride was not required in the leachant as a dissolution catalyst for the carbide particles but would be required if the particles contained ThO₂.

The leaching studies were conducted with unirradiated prototype Peach Bottom fuel that contained about 3% uranium and 14% thorium as carbon-coated ThC₂-UC₂ particles dispersed in a graphite matrix. The fuel was roll-crushed to -140 mesh, and small samples were leached with sufficient reagent to produce solutions 0.2 *M* in U + Th if all the uranium and thorium were dissolved. After leaching, the residues were washed thoroughly to ensure maximum recovery of solubilized uranium and thorium. In addition to determining the amounts of uranium and thorium leached, the leachate and wash solutions were analyzed for carbon, present in these solutions as soluble

organic compounds. The amount of carbon found in solution was compared with that originally present in the fuel, assuming that the carbon content (9.3%) of the $\text{ThC}_2\text{-UC}_2$ particles represented combined carbon (carbide).

In 5-hr leaches with boiling nitric acid solutions followed by water-washing of the residues, uranium recoveries increased from about 99.6 to 99.8% as the nitric acid concentration increased from about 2 to 13 M ; the corresponding increase in thorium recovery was from about 98 to 99.2% (Table 2). A similar behavior was noted with nitric acid solutions that were 0.05 M in HF. Uranium and thorium recoveries were not significantly increased by the addition of HF to the leachant. Slight, but possibly significant, increases in recoveries were obtained when the residues were washed with 10 M HNO_3 instead of water. These results, however, may merely show that the 5-hr leaching period is insufficient for maximum recovery of uranium and thorium. This hypothesis was fortified by other experiments in which the fuel was leached with two successive batches of fresh, boiling, 13 M HNO_3 . In these experiments, recovery of about 99.9% of both uranium and thorium was achieved.

The final solutions always contained soluble organic compounds, the products of the reaction of the $\text{ThC}_2\text{-UC}_2$ with nitric acid. The amount of carbon found in solution corresponded to 13 to 50% of the carbide carbon. The effect of the soluble organic compounds on feed-preparation procedures and on solvent extraction is being investigated. Preliminary results indicate that foaming is encountered in the Thorex feed adjustment operation.¹³ Earlier work with uranium carbides indicates that the organic material may cause emulsion formation and increased settling times during solvent extraction.¹⁴

Table 2. Uranium and Thorium Recoveries After Leaching
of Roll-Crushed Peach Bottom Fuel

Fuel crushed to -140 mesh. Boiling leachant used in each case.
Leaching time = 5 hr

Leachant Composition (M)		Wash	Recoveries (%)		Carbide Carbon in Leachate (% of original)
HNO ₃	HF		U	Th	
2.0	0	Water	99.6	98.2	24
5.0	0	Water	99.7	99.1	31
13.0	0	Water	99.8	99.2	13
15.8	0	Water	99.8	98.8	--
2.0	0.05	Water	99.8	96.9	50
5.0	0.05	Water	99.8	99.0	32
13.0	0.05	Water	99.8	99.4	--
13.0	0.05	Water	99.7	99.5	22
13.0	0.05	10 M HNO ₃	99.9	99.9	--
13.0	0.05	10 M HNO ₃	99.8	99.9	52

This was minimized by permanganate oxidation to destroy the organics. Investigations are under way to see if the Thorex feed preparation boildown will eliminate the objectionable organic material or if additional treatment will be required.

3.3 Engineering-Scale Leaching Studies

Preliminary experiments confirmed that fine grinding of Peach Bottom fuel to -140 mesh was necessary to rupture of all fuel particle coatings. Also, continuous, controlled addition of fuel to the acid in the leacher was found desirable to minimize foaming. After this, leaching equipment was built to process as much as 5 kg of ground fuel per batch as a slurry in 10 liters of leachant. The leacher was a heated 4-in.-diam vessel provided with an air-lift sparger and an external slurry recirculation line to provide good mixing. Crushed fuel was fed at a controlled rate to the leacher by a pneumatic transport system. The filter was a 6-in.-diam vessel with a granular-alumina-perforated-metal-plate filter cake support.

The flowsheet conditions and leaching results are summarized in Fig. 7 for the first experiment. The leaching acid contained fluoride; however, as noted in the laboratory studies, it was probably unnecessary. In the experiment, the rate of addition of ground fuel to the leacher was limited to about 75 g/min by the generation of foam from the initial reaction with the boiling acid. During the 7-hr reaction period, the ground fuel was kept suspended in the leacher by boiling and by the sparger. The slurry was then transferred by vacuum to the filter vessel, where the graphite residue was separated from the leach liquor and water washes by vacuum filtration. Solution samples taken during leaching showed that the concentration of dissolved carbon reached

Fig. 7. Engineering-Scale Grind-Leach Processing of Peach Bottom Fuel.

a peak value of about 3.5 g/liter in 1.5 hr (approximately 0.75 hr after adding all the graphite to the leacher) and slowly decreased to 1.15 g/liter at the end of the 7-hr leaching period.

The results of the first run indicated that 99.65% of the uranium and 99.33% of the thorium was recovered from the fuel, in good agreement with the results of laboratory work. Additional washing of a portion of the residue with hot 0.1 M HNO_3 showed that losses could be reduced slightly at the cost of approximately doubling the volume of the product and doubling the washing time. However, as noted in the laboratory leaching experiments, washing with concentrated acid may be more effective in reducing the losses to a very low level. The acid wash could then be used as the leachant for the next batch. Additional experimentation is under way.

3.4 Filtration of Graphite Slurries

Measurements of the permeability to 0.1 M HNO_3 of 1-to-2.5-ft-deep beds of the -140-mesh residue from the experiment described in Sect. 3.3 were correlated by the equation $V = 0.9 (\Delta P/L) (1/\mu)$, where V is the flow rate through the bed in $\text{gal. hr}^{-1} \text{ ft}^{-2}$; $(\Delta P/L)$ is the pressure drop through the bed in psi per ft of bed; and μ , the solution viscosity, is in centipoises (Fig. 8). The bed depth L can be calculated by assuming that the density of the graphite settled under 0.1 M HNO_3 is about 0.60 g/cm^3 , an average value determined in previous experiments. These results indicate that vacuum filtration will be satisfactory if the filter cake is not very deep. On the other hand, if other considerations such as criticality requirements dictate a small-diameter filter vessel, the resulting filter cake may be quite deep, thus making pressure filtration more attractive than vacuum filtration.

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Fig. 8. Permeability of Filter Cakes of -140 Mesh Leached Graphite to 0.1 M Nitric Acid.

4. BURN-LEACH PROCESS DEVELOPMENT FOR GRAPHITE-BASE HTGR FUELS

The burn-leach process (Fig. 9) for graphite-base HTGR fuel consists in crushing the fuel to a suitable size and feeding it to a fluidized-bed burner where the graphite and carbide carbon are converted to CO_2 and CO gases. The resulting fuel oxides are then dissolved in fluoride-catalyzed nitric acid and, after feed adjustment, uranium and thorium are recovered by solvent extraction. The fluidized-bed burner permits high combustion rates at relatively low temperatures, produces a free-flowing ash, and is easily operated.

Engineering feasibility of the burn-leach process was established in small-scale experiments with unirradiated fuel.¹⁵ The principal process problem is whether the burner off-gas can be decontaminated sufficiently to permit its release to the atmosphere. Hot-cell tests are currently under way at ORNL to demonstrate the process. The principal objective of these experiments is to determine the extent of volatilization of fission products into the off-gas and to test various methods for off-gas cleanup. Supplemental objectives are to determine the amount of fission product deposited on the burner surfaces and to study leaching, feed preparation, and solvent extraction performance.

As a guide to these experiments, the fission product activity of the burner off-gas was estimated¹⁶ for a plant processing HTGR fuel with a C/Th ratio of 200 and a $^{235}\text{U}/^{232}\text{Th}$ ratio of 0.068. The calculations were made for a burnup of 84,000 Mwd/ton, with 2100 days irradiation and 250 days of cooling. The fission products Kr, Ru, Te, Cs, Se, and Tc were found to be the only ones that would volatilize significantly as oxides during combustion. Since the composition of the burner off-gas

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Fig. 9. Burn-Leach Process for Graphite-Base Reactor Fuels.

determined experimentally¹⁵ (5% CO, 5% O₂, and 90% CO₂) is a nonequilibrium mixture, one cannot predict whether oxidation or reduction (by CO) of the fission products will have the predominating influence. Oxidizing conditions were assumed, since fission product volatilization is most likely to occur under this condition; and, hence, the fission product volatilization results predicted by calculation would tend to be conservative compared to those obtained in actual fluidized-bed combustion. The results of the calculations (Fig. 10) roughly substantiate tube furnace combustion experiments and indicate that appreciable volatilization of fission product oxides may occur at 750°C. If the off-gas is cooled to room temperature and passed through absolute filters before discharge, then ⁸⁵Kr will be the principal activity in the gas and will not normally represent an atmospheric disposal problem. Another tentative conclusion is that the fission products noted above may tend to reflux between the hot fluidized bed and the burner filters, thus creating a heating problem in the burner if allowed to accumulate indefinitely. Resolution of these problems must await the results of the hot-cell experiments; so it is premature to draw final conclusions from the preceding data.

5. ADSORPTION OF PROTACTINIUM ON UNFIRED VYCOR

Adsorption of protactinium on unfired Vycor has the capability of producing low-²³²U-content ²³³U from highly irradiated power reactor fuels. The process for recovering ²³³Pa by adsorption on unfired Vycor glass¹⁷ was demonstrated in hot-cell experiments with feeds prepared by dissolving sol-gel thoria fuel specimens in boiling 13 M HNO₃—0.05 M HF—0.1 M Al(NO₃)₃. The specimens had been irradiated

Fig. 10. Calculated Equilibrium Fission Product Content of Fluid Bed Burner Off-Gas (Oxygen pressure = 1 atm).

to about 5000 Mwd/metric ton in an average unperturbed neutron flux of 2.6×10^{14} and decayed 27 days.

As an example of the results obtained in the hot-cell runs, Fig. 11 shows the data obtained in an experiment with 100- to 120-mesh unfired Vycor. About 97% of the protactinium was adsorbed from a solution containing 126 mg Th per ml, 0.82 mg U per ml, 54 mg ^{233}Pa per liter, and 1.4×10^{12} gamma counts $\text{min}^{-1} \text{ml}^{-1}$. The solution was 11.4 *M* in HNO_3 , 0.05 *M* in HF, 0.1 *M* in $\text{Al}(\text{NO}_3)_3$ and was passed through a column 0.9 cm in diameter and 17 cm long containing 7 g of unfired Vycor. At a flow rate of about 1 ml/min, the column was loaded to 3.1 mg of ^{233}Pa per gram of glass. The loaded column had to be cooled with water to prevent boiling. The Vycor was washed with about eight column volumes of 10 *M* HNO_3 —0.1 *M* $\text{Al}(\text{NO}_3)_3$ at a flow rate of 0.5 ml/min. This removed 1.5% of the adsorbed protactinium. The remainder of the protactinium was then eluted with 0.5 *M* oxalic acid. The first 15 ml of product contained about 96% of the protactinium at an average concentration of 1.46 mg/ml or about 25 times the concentration of protactinium in the feed. The eluant sample having the peak ^{233}Pa concentration (2.86 mg/ml) had to be diluted to prevent boiling. The protactinium product was decontaminated for zirconium-niobium, rare earths, thorium, and uranium by factors of 5.5, 4.8×10^3 , $\geq 1 \times 10^4$, and $\geq 5.7 \times 10^2$, respectively. The ^{233}U which would be obtained from the decay of the protactinium would contain only about 0.1 to 0.5 ppm of ^{232}U .

Radiation appeared to have little or no effect on the unfired Vycor glass. A second experiment, using this same column, showed very nearly the same adsorption and stripping characteristics.

Fig. 11. Isolation of ²³³Pa by Sorption on 100-120 Mesh Unfired Vycor Glass.

In a more optimized process for recovering protactinium, the Vycor would probably be loaded to about 2.5 mg of ^{233}Pa per gram of glass to ensure 99% adsorption of the protactinium. This would result in slightly lower losses in the wash step and perhaps lower protactinium concentrations in the product but would have no effect on the product purity.

Other experiments showed that silica gel was slightly less effective and zirconium phosphate was only half as effective for protactinium recovery. Suitable stripping methods were not found for zirconium phosphate.

6. CLOSE-COUPLED PROCESS STUDIES

The gamma activity associated with daughters of both ^{233}U and ^{239}Pu recycled from power reactors necessitates shielding for fuel fabrication. Since this shielding is required, only a partial decontamination from fission products may be necessary during chemical processing. Fuel cycle cost reduction may also be achieved if processing and fabrication plants are close-coupled and perhaps located at the reactor station. The purpose of this program is to study simplified, low-cost, chemical processing methods that will yield a product decontaminated from fission products by a factor of about 1000 and that will be suitable as a feed for the sol-gel process for remote fuel refabrication. Initial emphasis is on the thorium fuel cycle; later we will consider the problems of liquid-metal-cooled fast-breeder reactors. The best application of close-coupled processing in the immediate future may be for the HTGR's; however, for initial evaluation of the principle of close-coupled processing, we are considering a conventional Zircaloy-clad $\text{ThO}_2\text{-UO}_2$ fuel for which processing technology is well developed.

6.1 Chemical and Equipment Development

The chemical development program initially consisted of evaluating processing methods other than solvent extraction to see if any would be more suitable for a close-coupled plant.¹⁸ A number of possible methods such as peroxide, oxalate, and phosphate precipitation, and electrodialysis, were investigated; however, anion exchange was the only method that gave promise of being developed into a workable process. However, resin capacity and decontamination were low, thus creating a recycle problem and requiring several cycles of anion exchange. It was concluded that solvent extraction is still the best choice for uranium and thorium recovery in a close-coupled plant such as the Thorium-Uranium Recycle Facility.

We then investigated a batch differential solvent extraction system to see if it was more suitable than continuous solvent extraction for a small plant. With 30% TBP in n-dodecane as the solvent and a feed that was 1.62 *M* Th, 0.13 *M* U, and 0.1 *M* acid deficient, more than 99.9% of the uranium and 48% of the thorium were extracted in 3.3 volumes of solvent. The decontamination factor of the uranium from gross gamma activity was 1400. Continuing the extraction until 9.8 volumes of solvent were used resulted in the extraction of 95% of the thorium and lowering the overall decontamination factor to 100. The remaining 5% of the thorium would have to be recycled to avoid lowering the overall decontamination factor below 100. Further testing showed that about 25% of the fluoride and about 40% of the zirconium dissolved in the leaching was extracted. The fluoride, in particular, would be highly undesirable in the reconstituted fuel. A high-thorium-content, dense, second organic phase will form in TBP extraction of thorium if the solubility of the TBP-thorium complex is exceeded. This

second phase was encountered in laboratory experiments but caused no difficulty. However, batch extraction tests in a small pulsed column were unsuccessful because an aqueous—second-organic-phase emulsion formed and the organic holdup in the column was excessive, even at very low throughput rates. For these and other reasons, we concluded that batch extraction for uranium and thorium recovery was undesirable. We are now concentrating on improving the continuous Thorex solvent extraction process.

6.2 Conceptual Plant Studies

A conceptual engineering design and preliminary economic evaluation was made for a small close-coupled plant for processing, at a rate of 165 kg/day, Zircaloy-clad, vibratorily-packed sol-gel (U-Th)O₂ fuel irradiated to at least 20,000 Mwd/metric ton. This particular capacity and fuel type (metal-clad oxide) was chosen to permit comparison of the close-coupled plant with a small on-site plant of similar capacity but for low-enrichment uranium fuel, very good decontamination of the products, and conventional direct fabrication. The ground rules and cost assumptions used in the close-coupled study were practically the same as those used in the small-plant study. In our study, it was assumed that batch-differential solvent extraction was used in the processing plant; when this proved impractical, the study was repeated to estimate costs for a single-extraction-cycle continuous-extraction system. We found that the difference in costs between the batch and the continuous processes was insignificant. The close-coupled plant was assumed to be fully integrated with a 1000-Mw (electrical) reactor station and included (1) underwater fuel element storage and dismantling;

(2) a remote maintenance shear-leach head-end, with feed adjustment, acid recovery, high-level off-gas treatment, and high- and low-level waste evaporation equipment in the same area; (3) solvent extraction with 30% TBP followed by sol preparation according to simplified method based on extraction, with a long-chain amine, of the nitrate from blended uranium and thorium nitrate product solutions; (4) gel formation, firing, sizing; and (5) fuel fabrication in an adjoining remotely operated facility similar in design to TURF.¹⁹ Capital costs for the processing plant were estimated²⁰ from preliminary conceptual equipment and building layouts; operating costs were derived by adjusting published data²¹ to an integrated facility of relatively small size and adding perpetual care waste storage charges derived from computer calculations.²² Capital costs for the fabrication plant were estimated by computer²³ and operating costs for the fabrication plant were estimated on roughly the same basis as for the chemical plant. Fully developed technology was assumed and a frugal approach was used on plant staffing and overhead.

The processing and remote fabrication cost (Table 3) of \$156/kg (U + Th) cannot be compared with today's costs because experience is not available for remote fabrication. However, the processing cost component is estimated to be about \$75/kg (U + Th) compared to the published NFS price²¹ of about \$78/kg (U + Th) for processing the Indian Point Reactor ThO₂ core. This comparison is encouraging, considering that the close-coupled plant throughput is one-third of the NFS rating for thorium and the processing product is a denitrated, mixed U-Th sol suitable for gel formation. However, the thorium fuel cycle still costs more than low-enrichment uranium. For example, the small on-site plant study²⁴ estimated a cost of \$120/kg of low-enrichment uranium.

Table 3. Capital and Operating Costs for a Small
Close-Coupled Processing Plant

Capital Cost

Processing building and equipment	\$ 7,430,000
Fabrication building and equipment	5,300,000
Startup cost, processing plant ^a	1,420,000
Startup cost, fabrication plant ^a	1,448,000

Total capital investment	\$15,598,000
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Annual Operating Cost^b

Capital amortization at 22-1/2% per year	\$ 3,510,000
Processing plant (direct costs)	1,420,000
Fabrication plant (direct costs)	2,556,000
Solid waste	75,000
High-level waste storage	282,000
Medium-level waste storage	153,000

Total annual operating cost	\$ 7,996,000
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\$156/kg (U + Th)

^a One year's operating cost, excluding waste storage and fuel element hardware.

^b Exclusive of inventory charges and cost for U + Th makeup.

This indicates that the more complex thorium processing system and remote fabrication for metal-clad oxide fuel costs about 30% more than low-enrichment uranium oxide fuel using high-decontamination processing and direct fabrication. Thus, it appears that the future of the thorium cycle lies with the advanced converters, such as the HTGR, where the unique advantages of thorium as a fuel can be realized. Extra head-end costs, perhaps amounting to as much as \$134/kg (U + Th) in the case of HTGR fuels,¹⁵ may be charged for processing in existing plants. Therefore, we think that small close-coupled plants may be a desirable interim solution to minimize cost disadvantages of thorium fuel until large central thorium fuel cycle plants can be justified.

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